TECHNICAL GUIDANCE DOCUMENT
INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

Determining the Fraction of Organic Carbon

for Development of Site-Specific Screening Levels

Office of Land Quality

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Background

Soil is a complex mixture of mineral-derived compounds and organic matter. The ratios of each component can vary widely depending on the type of soil. Soil organic matter is a term used by agronomists for the total organic portion of the soil that is derived from decomposed plant matter, microorganisms, and animal residues. The decomposition process can create complex high molecular weight biopolymers (e.g., humic acid) as well as simpler organic compounds (decomposed lignin or cellulose). Only the simpler organic compounds contribute to the fraction of organic carbon.

There is no rigorous definition of the fraction of organic carbon (*Foc*). *Foc* is, in general terms, the portion of the organic matter that is available to adsorb the organic contaminants. The higher the organic carbon content, the more organic contaminants may be adsorbed to the soil and the less of those contaminants will be available to leach to the ground water. The Remediation Closure Guide (RCG) allows collection of site-specific *Foc* samples to calculate a site-specific migration to ground water screening level. In the Soil to Ground Water Partition Model, the coefficient, K_d, for organic compounds is the *Foc* multiplied by the chemical-specific soil organic carbon water partition coefficient, K_{oc}.

Typical Indiana surface soils have 1-6% soil organic matter (SOM), depending on soil type. Since organic carbon comprises about 58% of the SOM, the upper range of *Foc* for fertile surface soil is expected to be less than approximately: 6% SOM * 0.58 = 3.42% (0.0342 g/g) organic carbon. Subsurface soils are expected to be much lower in organic matter. The EPA's Soil Screening Users Guidance recommends 0.2% (0.002 g/g) as the default concentration of organic carbon for subsurface soils. Site-specific *Foc* data should accompany site-specific migration to groundwater remediation screening levels.

Sampling for site-specific *Foc* values should follow background procedures (Section 6 of the RCG). Therefore, samples from borings should be collected from an area unaffected by a release, i.e., not in a contaminated area. Samples must be taken from the same types of soil or strata that are at, and below, the contaminated soil. Analyze each sample in triplicate. The *Foc* for the site is the mean of all the samples. Submitted results should include boring locations and boring logs, and the soil series and map unit from the USDA County Soil Survey. Results are subject to IDEM approval. **Samples should also be analyzed for the contaminants of concern to demonstrate that the *Foc* samples are not contaminated.**

Sample Handling and Pretreatment

There should be no extraneous organic matter in the sample, e.g., roots, sticks, wood, paper, or biota. Samples should be air-dried and large chunks of sample pulverized to pass through a Number 10 (2 mm) sieve.

Indiana soils derived from glacial till are calcareous and require pretreatment to remove inorganic carbon prior to analysis. For the dichromate oxidation methods, this can be done by addition of an acid to the soil sample. HCl should be avoided because it introduces Cl^-, an interferent. A suitable pretreatment acid is a combination of H_2SO_4 and $FeSO_4$ (Schumacher, 2002; Nelson and Sommers, 1996).

Analytical Methods for *Foc*

Two analytical methods are commonly used: the Walkley-Black Method, a wet dichromate oxidation method and ASTM D2974, a dry oxidation method. IDEM recommends the use of the Walkley-Black Method. However, comparable methods are acceptable. The dichromate oxidation method is, however, appropriate for determining the low concentrations of organic carbon expected in Indiana subsurface soils.

Note, EPA Method SW 846-9060A TOC and EPA Method MCAWW-415.1 are water methods and are not acceptable for determining organic carbon in soil.

Dichromate Oxidation Method (Walkley-Black)
The Walkley-Black method is most appropriate for subsurface soil samples in Indiana. This wet chemistry technique can be divided into two phases: sample extraction (oxidation) and sample quantitation. There are two variations on the basic dichromate oxidation (extraction) of the sample. The Walkley-Black oxidation relies upon the heat of solution of the sulfuric acid and water for the reaction. This method incompletely oxidizes the organic carbon and a correction factor of 1.3 is commonly applied to the results to adjust the easily oxidizable carbon to total organic carbon. The second variation entails heating the reaction mixture for a specified time period to achieve complete oxidation of the organic carbon. No correction factor is needed for this variation. (Mebius, 1960; Tinsley, 1950; Kalembasa & Jenkinson, 1973; and others).

The unreacted dichromate should be determined by titration with ferrous ammonium sulfate to a potentiometric endpoint with an automated titrator. The spectrophotometric method described by Sims & Haby, 1971 is an acceptable alternative to titration. Manual titration to the color change endpoint is less precise and not recommended. Consult with IDEM OLQ Chemistry Services Section staff if you have any questions about particular methods and details.

Due to the small amount of soil used in each analysis, each sample should be analyzed in triplicate to obtain an estimate of how precise the measurement is. A reagent blank should be prepared and analyzed along with each sample set. Laboratory control spike/spike duplicates should be analyzed with each analytical batch of 20 or fewer samples. Standard reference materials should be analyzed along with the samples. In addition, the percent moisture should be determined from a separate sample and the results reported on a dry weight basis.

Documentation Requirements
Documentation should include the *sampling-related items, laboratory-related items*, and elements for Full QA/QC listed in Section 3.9 and Table 3-A of the RCG. The specific method should be cited as well as details of the analytical procedures. Because there may be procedural variations among laboratories, a copy of the laboratory's SOP for the method should be submitted with the data package. Documentation should include the boring logs and soil type as described in the USDA County Soil Survey.

Analytical Deliverables in Addition to Section 3.9

- Sample pre-treatment and/or particle size reduction
- Date and time of Analysis
- Lab sheets Showing
    - Weight of sample
    - Volume and normality (or molarity) of dichromate solution
    - Volume and normality (or molarity) of titrant
    - Reaction time
    - Temperature of reaction (if reaction is heated)
- Blank results determining concentration of titrant
- Moisture content of soil samples
- Average of each *Foc* sample (triplicate analyses) in dry weight
- Percent relative standard deviation (% RSD) of triplicate analyses
- Average *Foc* of each soil strata

References
Burt, Rebecca, Ed. Soil Survey Laboratory Methods Manual, Natural Resources Conservation Service, Soil Survey Investigations Report No. 42, Version 4.0, November 2004.

Mebius, L.J. 1960. A Rapid Method for the Determination of Organic Carbon in Soil. Anal Chim. Acta. 22:120-124.

Kalmebasa, S.J., and D.S. Jenkinson, 1973. A Comparative Study of Titrimetric and Gravimetric Methods for the Determination of Organic Carbon in Soil. J. Sci. Food Agric. 24:1085-1090.

Nelson, D.W. and Sommers, L.E. 1996. Chapter 34, Total Carbon, Organic Carbon and Organic Matter, *In* Sparks, D.L. Ed. Methods of Soil Analysis Part 3 – Chemical Methods. Soil Science Society of America and American Society of Agronomy, 677 S Segoe Rd, Madison, WI 53771, 1996.

Remediation Closure Guide, March 22, 2012 with corrections through July 9, 2012

Schulte, E.E. 1995. Chapter 8 Recommended Soil Organic Matter Tests. *In* Recommended Soil Testing Procedures For The Northeastern United States, 2nd Ed., Northeastern Regional Publication No. 493. Cooperative Extension, University of Delaware College of Agriculture & Natural Resources.

Schumacher, Brian A. 2002. Methods for the determination of total organic carbon (TOC) in soils and sediments. USEPA Environmental Sciences Division National Exposure Research Laboratory, Ecological Risk Assessment Support Center, Office of Research and Development, Las Vegas, NV.

Sims, J.R. and V.A. Haby. 1971. Simplified colorimetric determination of soil organic matter. Soil Sci. 112:137-141.

Tinsley, J. 1950. Determination of organic carbon in soils by dichromate mixtures. P. 161-169. *In* Trans. 4th Int. Congr. Soil Sci., Vol. 1 Hoitsemo Brothers, Groningen, the Netherlands.

U.S. EPA. Soil Screening Guidance: User's Guide. EPA/540/R-96/018, April 1996.

Walkley, A., and Black, I.A. 1934. An examination of the Degtijareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37:29-38.